



Case II/2-22774

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF
VERONIQUE HALL-GOULLE ET AL.
SERIAL NO. 10/531905

Group Art Unit: 1796

Examiner: AMINA S. KHAN

FILED: April 18, 2005

FOR: PROCESS FOR INCORPORATION OF UV-LUMINESCENT COMPOUNDS IN POLYMERIC
MATERIALS

Commissioner of Patents and Trademarks
Washington, D.C. 20231

DECLARATION UNDER 37 CFR 1.132

I, Véronique Hall-Goulle, a citizen of the Republic of France, residing in 4143 Dornach, Switzerland, hereby declare:

That I was awarded the degree of Docteur de l'Université Louis Pasteur (organic chemistry), Strasbourg / France, in 1992;

In addition to 3 years of experience in the field of supramolecular chemistry, I have more than 15 years of experience in the field of dyes and pigments research within Ciba Inc. (former Ciba Specialty Chemicals Inc. and CIBA-GEIGY AG), Basle, Switzerland, being particularly involved in the synthesis of new functionalized chromophores, latent pigments, fluorescent dyes, lanthanide complexes, as well as application research in the fields of textile and inks.

That the experiments described in the following have been carried out under my supervision and the evaluation of the test results has been done by myself.

That I am a co-inventor of the present U.S. Application Serial No. 10/531905; and that I am familiar with the subject-matter thereof.

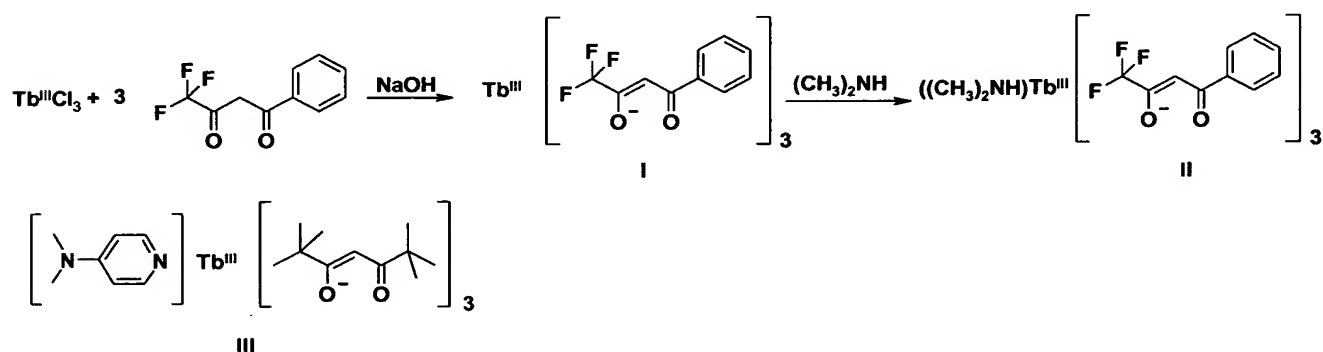
That I am familiar with the subject matter of the state of the art WO 96/20942, US 5,837,042, US 4,891,505 and US 4,655,788.

TEST REPORT

Comparative examples 1 to 6 show the superiority of complex III (according to the invention) over complex II (state of the art) in the application of conventional aqueous exhaust dyeing of polyester (PES). In identical conditions, the fluorescence obtained under UV lamp from the resulting dyed threads is significantly stronger with application of III (according to the invention) in comparison to II (state of the art).

Complex II is described in Example 1 of US 4,655,788. As US 4,655,788 does not disclose the exact stoichiometry, the structurally closest compound was synthesised, namely the complex with three anionic ligands ($n = 3$). Complex II is structurally more closely related to complex III than the compound of example 1 of US 4,891,505, which contains four anionic ligands ($n=4$). Complex II is encompassed by colorant comprising a rare earth metal and a chelating ligand of US 4,891,505.

Complex III is described in WO 96/20942 as compound A1 and is described in the present application and is according to the present invention.



Example 1 - Preparation of intermediate tris-complex I

To a solution of 20.00g of Benzoyl-1,1,1-Trifluoroacetone dissolved in 75 mL of a 1/1 mixture of ethanol and water is added dropwise at room temperature 24mL of an aqueous solution of 4N sodium hydroxide. After 15 minutes of stirring, a solution of 11.51g of Terbium chloride hexahydrate is added dropwise at such a rate that the exothermy is kept at 35°C at the maximum. The yellowish reaction mixture is stirred for 2.5 hours and concentrated on a rotary evaporatory. Filtration (porosity 4) of the concentrate affords a first portion of product with is rinsed with ethanol and dried in a vacuum oven overnight. Similarly evaporation of the filtrate affords the remaining major portion of tris-complex I which is in turn dried in a vacuum oven overnight.

Example 2 - Preparation of complex II

18.00g of tris-complex I and 3.50g of dimethylamine (33% in ethanol) are added to 50mL of ethanol at room temperature. After heating to reflux for 1.5 hours, the clear hot reaction mixture is filtered (porosity 4) and the filtrate evaporated to dryness on a rotary evaporatory. Hexane is added to the remaining oily substance and after stirring at room temperature for several hours, the resulting precipitate is collected by filtration (porosity 4) and dried at 60°C in a vacuum oven to finally afford 8.29g of the terbium complex II as a beige powder.

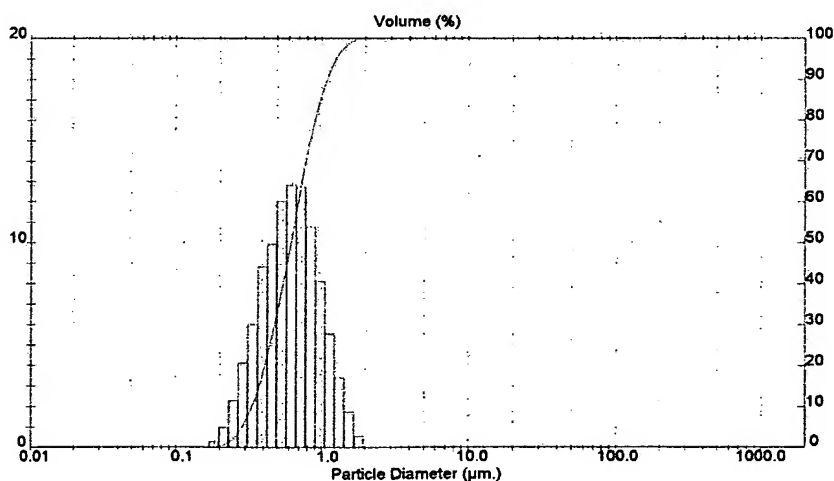
Differential Scanning Calorimetry of (II) (30.0-300.0°C at 10°C/min): melting point=176.27°C

Example 3 - Preparation of an aqueous dispersion of complex II

A formulation is prepared in a glass bottle containing 5.24g of complex II, 2.77g of Narlex DX2020 (35%), 0.31g of Surfynol 104 PG-50 and 13.44g of deionised water.

80.00g of Zircomium beads (diameter 0.6 to 1mm) are added to the preparation and the tightly closed bottle is placed in a Scandex apparatus and agitated for 10 hours. The thus obtained fine dispersion is then filtered on a conventional Büchner funnel to provide 15.52g of the desired final dispersion of complex II.

The particle size distribution of the dispersion is measured with a MALVERN instrument and the histogram is represented below.



Example 4 - Exhaust dyeing of PES thread with dispersion of complex II

For 40g of PES thread (single thread, 17 Tex), the dyeing bath is composed of 800mL water (liquor ratio 1/20), 2.40g of Cibatex AB 45, 0.80g of Univadine Top, 0.40g Cibafluid CD, 0.40g of Cibafluid FFW, 4,00g of Lutensol. 8.30g of the above described dispersion of complex II is added

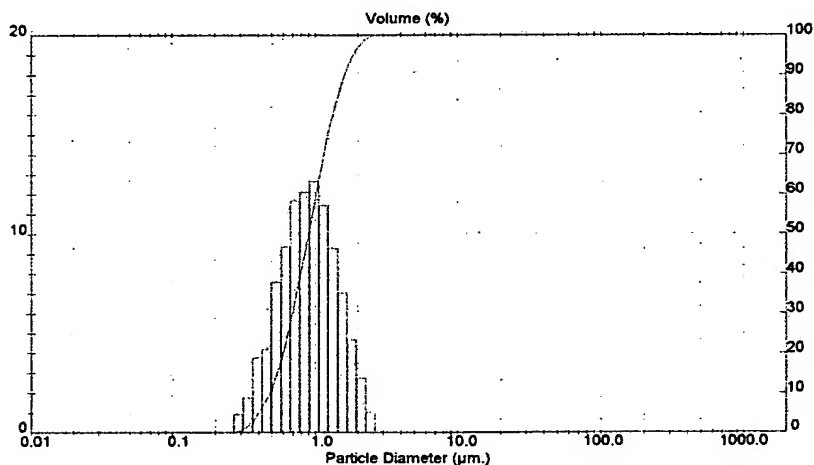
at 50°C over 5 minutes, after which the turbocolor apparatus is closed and its operating temperature is further raised up to 135°C by a gradient of 2°C *per* minute. After a further dyeing period of 1 hour at 135°C, the system is rinsed. Reduction cleaning is performed by addition of 3.20g caustic soda 36°Bé, 1.60g hydrosulphite concentrated and 0.80g Eriopon OS, and finally neutralisation with 1.6mL acetic acid (80%).

Example 5 - Preparation of an aqueous dispersion of complex III

In a similar way to Example 3, a formulation is prepared in a glass bottle containing 4.99g of complex III, 3.00g of Narlex DX2020 (35%), 0.34g of Surfynol 104 PG-50 and 13.59g of deionised water.

80.00g of Zircomium beads (diameter 0.6 to 1mm) are added to the preparation and the tightly closed bottles placed in a Scandex apparatus and agitated for 10 hours. The thus obtained fine dispersion is then filtered on a conventional Büchner funnel to provide 16.85g of the desired final dispersion of complex III.

The particle size distribution of the dispersion is measured with a MALVERN instrument and the histogram is represented below.



Example 6 - Exhaust dyeing of PES thread with dispersion of complex II

In a similar way to Example 4, for 40g of PES thread (single thread, 17 Tex), the dyeing bath is composed of 800mL water (liquor ratio 1/20), 2.40g of Cibatex AB 45, 0.80g of Univadine Top, 0.40g Cibafluid CD, 0.40g of Cibafluid FFW, 4.00g of Lutensol. 8.00g of the above described dispersion of complex III is added at 50°C over 5 minutes, after which the turbocolor apparatus is closed and its operating temperature is further raised up to 135°C by a gradient of 2°C *per*

minute. After a further dyeing period of 1 hour at 135°C, the system is rinsed. Reduction cleaning is performed by addition of 3.20g caustic soda 36°Bé, 1.60g hydrosulphite concentrated and 0.80g Eriopon OS, and finally neutralisation with 1.6mL acetic acid (80%).

Example 7 – Comparison between example 4 and example 6

The photographs reproduced in Figure 1 and Figure 2 below demonstrate the difference in fluorescence under UV light (254nm) between the final application by conventional PES exhaust dyeing of the two terbium complexes II and III respectively (example 4 vs. example 6):



Figure 1. Example 4 (right) and example 6 (left) under daylight exposure.

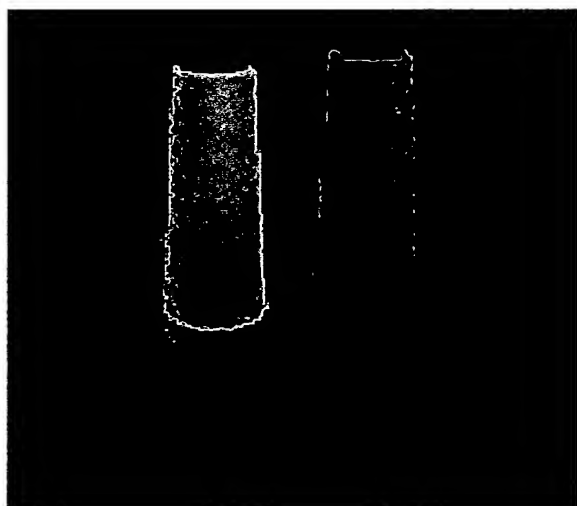


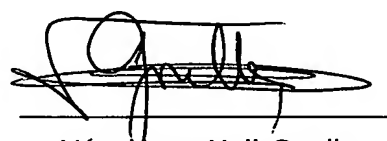
Figure 2. Example 4 (right) and example 6 (left) under UV light (254nm).

Discussion of Results

This comparative test shows that fibres treated with the process of the invention (structure III) exhibit a considerable stronger fluorescence under UV radiation than fibres treated with the state of the art analogous compound (structure II). This finding is surprising and could not be expected as a person skilled in the art considered the lanthanide chelates of WO 96/20942, US 5,837,042, US 4,891,505 and US 4,655,788 as equivalent at the time this invention was made.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

Signed, this 17th of June 2008



Véronique Hall-Goulle